

PATENT SPECIFICATION

(11) 1 232 098

1 232 098

NO DRAWINGS

- (21) Application No. 39079/68 (22) Filed 15 Aug. 1968
 (31) Convention Application No. P 16 44 472.7
 (32) Filed 16 Aug. 1967
 (31) Convention Application No. P 17 69 078.7
 (32) Filed 29 March 1968 in
 (33) Germany (DT)
 (45) Complete Specification published 19 May 1971
 (51) International Classification C 09 b 57/00
 (52) Index at acceptance
 C4P D1S
 C3R 2C11 2C12 2C13P 2C14B 2C25 2C9Q 2L2X 2L6G
 C4A C12A C12B C12C C12G C14 C7 C9A



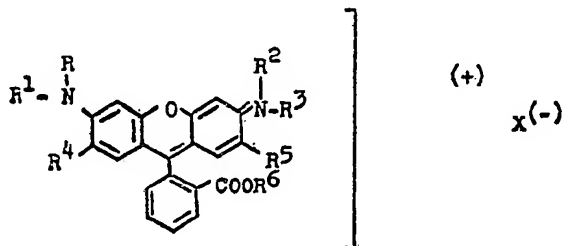
(54) RHODAMINE DYES WHICH ARE SPARINGLY SOLUBLE
OR INSOLUBLE IN WATER

(71) We, BADISCHE ANILIN- & SODA-FABRIK AKTIENGESELLSCHAFT, a German Joint Stock Company, of Ludwigshafen/Rhein, Federal Republic of Germany, do hereby declare the invention, for which we pray that a Patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

Rhodamine dyes are outstandingly suitable for making printing inks (flexographic printing inks, glycol printing inks and the like), stamping inks, marking inks and ball point pen inks or for example for coloring transparent surface coatings, because of their high color strength and brilliance. However, since the conventional rhodamine dye chlorides or sulfates are easily soluble not only in alcohols and glycols but also in water, dyeings and prints prepared therewith generally have only low water fastness. For use in flexographic printing inks it is possible to add auxiliaries such as precipitants or acid resins which effect fixing so as to improve the water fastness. Examples of precipitants are high molecular weight organic acids. For many other purposes, for example in the production of ball point pen ink, glycol printing ink or transparent surface coatings, it is not possible, however, to add these auxiliaries so that the water fastness of the colorations is often very low.

Moreover the commercial salts of rhodamine dyes, i.e. the chlorides or sulfates, are in some cases only of moderate solubility in alcohols and glycols so that it is often impossible to prepare highly concentrated solutions which will remain stable even after prolonged storage. Another disadvantage of the chlorides and sulfates is their very marked corrosive effect on the metal parts of storage vessels and processing machines.

We have now found that rhodamine dyes, having the general formula:—



in which:

R denotes a hydrogen atom or a methyl or ethyl group,
 R¹ denotes a hydrogen atom or a methyl or ethyl group,
 R² denotes a hydrogen atom or a methyl or ethyl group,
 R³ denotes a hydrogen atom or a methyl or ethyl group,

R^4 denotes a hydrogen atom or a methyl group,
 R^5 denotes a hydrogen atom or a methyl group,
 R^6 denotes a hydrogen atom or a methyl or ethyl group and

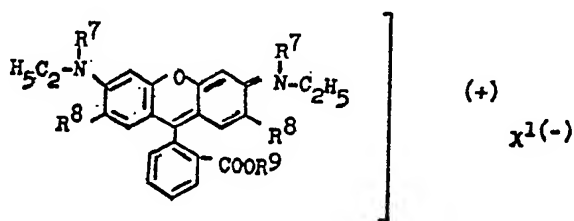
5 $X^{(-)}$ denotes the anion of a sulfuric acid monoester or an aliphatic sulfonic acid or a benzene sulfonate, toluene sulfonate, xylene sulfonate, $NO_3^{(-)}$, $H_2BO_3^{(-)}$, $HCO_3^{(-)}$, $H_2PO_4^{(-)}$, $HCrO_4^{(-)}$ or $HCr_2O_7^{(-)}$ anion, are sparingly soluble or insoluble in water and only exhibit the said disadvantages to a slight extent or not at all.

10 Specific examples anions of sulfuric acid monoesters or of aliphatic or aromatic sulfonic acids are methosulfate, ethosulfate, ethylhexanesulfonate, benzenesulfonate, toluenesulfonate or xylenesulfonate anions.

Rhodamine dye salts having the anions $NO_3^{(-)}$, $HCO_3^{(-)}$, $H_2BO_3^{(-)}$ and $H_2PO_4^{(-)}$, or methosulfate, ethosulfate, benzenesulfonate, toluenesulfonate and xylenesulfonate are particularly valuable.

15 Particular sub-classes of dyes according to the invention include those compounds in which not more than one of R^2 , R^3 and R^5 and not more than one of R , R^4 and R^6 denote hydrogen those in which R^2 and R^3 each denote a methyl or ethyl group and those in which R^4 and R^5 each denote a methyl group.

A preferred group of rhodamine dyes have the general formula: —



20 in which:

R^9 denotes a hydrogen atom, a methyl or ethyl group,

R^7 denotes a hydrogen atom or an ethyl group,

R^8 denotes a hydrogen atom or a methyl group and

25 $X^{(-)}$ denotes an $NO_3^{(-)}$, $HCO_3^{(-)}$, $H_2BO_3^{(-)}$, $H_2PO_4^{(-)}$, $CH_3OSO_3^{(-)}$, $C_6H_5SO_3^{(-)}$, $CH_3CH_2OSO_3^{(-)}$ or $CH_3C_6H_4SO_3^{(-)}$ anion.

It is surprising that the new rhodamine salts should be sparingly soluble or insoluble although the alkali metal salts having these anions, as well as the chlorides and sulfates, are readily soluble. Owing to their sparing solubility in water (which results in an improvement in the fastness to water of dyeings and prints and the like) and the simultaneous improvement in solubility in alcohols such as methanol, ethanol, propanol or benzyl alcohol, glycols such as ethylene glycol, diethylene glycol, triethylene glycol, propylene glycol or dipropylene glycol, glycol monoalkyl or dialkyl ethers or aryl ethers and polyglycol ethers, the new dyes are eminently suitable for the applications enumerated above. It is possible, however, although not necessary, to use compounds known as precipitants or fixing resins.

35 The dyes may be used also for the production of highly concentrated solutions which are stable in storage and which may be used for example as stock solutions for the preparation of printing inks, stamping inks or marking inks.

40 The new dye salts corrode metal parts much less than commercial dye salts do. The rhodamine dyes are produced by known methods, for example by reaction of the dye bases with the appropriate acids, by double decomposition of dissolved rhodamine chlorides or sulfates with the alkali metal salts of the acids to which the anions belong or by reaction of the chlorides or sulfates with sulfonic acids.

45 The following Examples, in which parts and percentages referred to are by weight, describe advantageous methods.

EXAMPLE 1

50 10 parts of N-diethyl-meta-aminophenol is heated with 12 to 13 parts of phthalic anhydride for four to five hours at 170° to $175^\circ C$. The melt, while still hot, is introduced into 70 parts of an about 10% aqueous caustic soda solution and stirred in the cold for about forty hours. After the product has been filtered off and washed with water, about 12 to 12.3 parts of rhodamine base B (with reference to a 100% product) is obtained. The moist rhodamine base is then dissolved in 100 parts of hot

water by adding 1.5 parts of 76% sulfuric acid and clarified by filtration. A solution of 5.4 parts of para-toluenesulfonic acid (89%) in 10.8 parts of water at 60°C is allowed to flow slowly, while stirring well, into the dye solution which is still at 60°C. The whole is allowed to cool and the crystals formed suction filtered, washed with water until free from acid, dried at 80°C and 16.0 to 16.5 parts (93.6 to 96.5% of the theory) of green, sparingly soluble rhodamine B para-toluenesulfonate is obtained.

In order to prepare a glycol printing ink which stores very well and which has scarcely any corrosive effect, 10 parts of the ground rhodamine B para-toluenesulfonate is dissolved in 90 parts of a mixture of 36 parts of a cyclohexanone condensation product and 54 parts of diethylene glycol at 95°C.

The fastness to water of prints prepared with this printing ink is better than when commercial rhodamine B chloride (C.I. 45,170) is used as a dye.

EXAMPLE 2

The procedure of Example 1 is followed but a solution of 4.4 parts of benzene sulfonic acid in 8.8 parts of water at 60°C is used instead of a solution of 5.4 parts of 89% p-toluenesulfonic acid in 10.8 parts of water at 60°C. 15.9 parts (95.2% of the theory) of rhodamine B benzenesulfonate which is sparingly soluble in water is obtained which may also be used, as in Example 1, for the production of a glycol printing ink.

Rhodamine B xylenesulfonate and rhodamine B ethylhexanesulfonate (prepared analogously) are also suitable for the said purpose.

EXAMPLE 3

13.3 parts of rhodamine B extra (C.I. 45,170) is dissolved in 100 parts of water at 80°C and then at 60°C a solution of 5.0 parts of sodium benzenesulfonate in 26.6 parts of water is slowly added with good stirring. After the whole has cooled, the green, sparingly soluble crystals formed are suction filtered, washed with water until they are free from salt and dried at 80°C. 15.8 to 16.1 parts (94.5 to 96.4% of the theory) of rhodamine B benzene-sulfonate is obtained.

16.2 to 16.4 parts (94.8 to 95.9% of the theory) of well crystallized sparingly water-soluble green rhodamine B para toluenesulfonate is obtained analogously from 13.3 parts of rhodamine B extra with a solution of 5.4 parts of sodium para-toluenesulfonate in 26.6 parts of water.

EXAMPLE 4

10 parts of 3,6-bis-(ethylamino)-2,7-dimethylfluoran is introduced into 50 parts of methanol and the 10 parts of concentrated sulfuric acid is added to the suspension. The whole is boiled for four to five hours under reflux, the excess of methanol is distilled off and the residue is taken up in 250 parts of hot water. It is filtered at about 90°C from nonesterified bases and then at 60°C to 70°C a solution at 60°C of 4.5 parts of para-toluenesulfonic acid (89%) in 9.0 parts of water is allowed to flow slowly with good stirring into the solution of the dye hydrogen sulfate at 60°C to 70°C. After the whole has cooled, the product is suction filtered, washed free from acid with water, dried at 80°C and 13.1 to 13.5 parts (94 to 97% of the theory) of sparingly water-soluble 3,6 - bis - (ethylamino) - 2,7 - dimethyl - 9 - (2' - carbomethoxyphenyl)-xanthylumparatoluenesulfonate is obtained.

13.4 to 13.8 parts (94 to 97% of the theory) of the sparingly water-soluble 3,6 - bis - (ethylamino) - 2,7 - dimethyl - 9 - (2' - carboethoxyphenyl) - xanthylum-para - toluenesulfonate is obtained in the same way when ethanol is used instead of methanol.

8 parts of the 3,6 - bis - (ethylamino) - 2,7 - dimethyl - 9 - (2' - carboethoxyphenyl) - xanthylumpara - toluenesulfonate thus obtainable and 25 parts of shellac are dissolved at room temperature in 90 parts of commercial ethanol and 10 parts of ethylene glycol monoethyl ether. A flexographic printing ink having very good storage stability is thus obtained. Prints prepared with it have an excellent fastness to water determined in accordance with German Standard DIN 16,524. This ink is much better than the product obtained when commercial rhodamine 6G ethyl ester chloride (C.I. 45,160) is used.

When alkylsulfonates, benzenesulfonates and xylenesulfonates of 3,6 - bis - (ethylamino) - 2,7 - dimethyl - 9 - (2' - carbomethoxyphenyl) - xanthylum or 3,6 - bis - (ethylamino) - 2,7 - dimethyl - 9 - (2' - carboethoxyphenyl)xanthylum cations, which can be prepared in a manner analogous to that described in Example 4, are used to make flexographic printing inks, similar results are achieved.

EXAMPLE 5

When methylsulfuric acid or ethylsulfuric acid is used for esterification of 3,6-bis - (ethylamino) - 2,7 - dimethylfluoran analogously to Example 4, the rhodamine 6G methyl ester methosulfate or rhodamine 6G methyl ester ethosulfate is obtained after appropriate working up, or the corresponding salts of the ethyl esters when using ethanol. These sparingly water-soluble dye salts may be termed according to the nomenclature 3,6 - bis - (ethylamino) - 2,7 - dimethyl - 9 - (2' - carbomethoxyphenyl) - xanthylium methosulfate (=rhodamine 6G methyl ester metho sulfate) or 3,6 - bis - (ethylamino) - 2,7 - dimethyl 9 - (2' - carbomethoxyphenyl) - xanthylium ethosulfate (=rhodamine 6G methyl ester ethosulfate). The same is true of the ethyl esters.

To prepare a red ball point pen in which is very stable in storage and has good writing qualities, 20 parts of rhodamine 6G ethyl ester ethosulfate is dissolved at 90°C in a solution of 25 parts of a hexanetriol phthalate in 55 parts of ethylene glycol monophenyl ether.

When rhodamine 6G methyl ester methosulfate is used instead of rhodamine 6G ethyl ester ethosulfate, a red ball point pen ink which has very good storage stability and good writing qualities is obtained in a similar way.

EXAMPLE 6

10 parts of rhodamine 6G ethyl ester ethosulfate prepared as described in Example 5 is introduced at room temperature into a mixture of 12.6 parts of ethylene glycol monophenyl ether and 2.4 parts of ethylene glycol. The whole is heated to 85°C and the mixture is kept at this temperature for four to five hours, after which it is cooled to room temperature and suction filtered. 24.5 parts of a 40% solution of rhodamine 6G ethyl ester ethosulfate is obtained whose color strength as compared with commercial rhodamine 6G ethyl ester chloride (C.I. 45,160) (powder) is 33% according to spectrophotometric measurement. The highly concentrated rhodamine 6G solution thus prepared is distinguished by good storage stability and may be used, because no dust is formed, as a stock solution for the production of printing inks, stamping inks or marking inks.

EXAMPLE 7

10 parts of rhodamine 6G ethyl ester ethosulfate prepared as described in Example 5 are introduced into 10 parts of an about 10% aqueous caustic soda solution and stirred for about forty hours in the cold. After the product has been filtered off and washed with water, 11.5 parts of rhodamine base B is obtained with reference to a 100% product. The moist rhodamine base is then dissolved in 10 parts of water with the addition of 0.15 parts of 76% sulfuric acid while hot and clarified by filtration. 0.5 parts of concentrated hydrochloric acid is added and then while cooling, 0.46 parts of concentrated nitric acid is added while stirring. Following the cooling, suction filtration is carried out and the product is washed with water until free from acid, dried at 90°C and 15 parts of green water-insoluble rhodamine B nitrate is obtained.

5 parts of rhodamine B nitrate and 25 parts of shellac are dissolved in 90 parts of commercial ethanol and 10 parts of ethylene glycol monoethyl ether at room temperature to make a flexographic printing ink having good storage stability.

The fastness to water of prints prepared with it is better than when commercial rhodamine B chloride (C.I. 45,170) is used as the dye.

EXAMPLE 8

The procedure of Example 7 is followed but 0.45 parts of sodium bichromate is used instead of 0.46 parts of concentrated nitric acid. About 20 parts of water-insoluble rhodamine B bichromate is obtained which may also be used for the production of flexographic printing inks according to Example 7.

The dyes rhodamine B chromate and rhodamine B borate which can be prepared in an analogous manner are also suitable for this purpose.

EXAMPLE 9

10 parts of 3,6 - bis - (ethylamino) - 2,7 - dimethyl - 9 - (ortho - carboxyphenyl) - xanthene is introduced into 50 parts of methanol and then 10 parts of concentrated sulfuric acid is added to the suspension. The whole is heated to boiling point under reflux for four to five hours, the alcohol is distilled off and the residue is taken up in 250 parts of hot water. Unreacted base is filtered off at about 90°C and then 7.9 parts of concentrated phosphoric acid (85%) is added while stirring

at 60° to 70°C, following which the phosphate of rhodamine 6G methyl ester crystallizes out during cooling, is filtered off at room temperature, washed with water and dried at 80° to 90°C. 13 to 14 parts of the dye salt is obtained.

When 7.9 parts of 85% phosphoric acid and ethanol are used instead of methanol 13 to 14 parts of 3,6 - bis - (ethylamino) - 2,7 - dimethyl - 9 - (2' - carboethoxyphenyl) - xanthylum phosphate is obtained in the same way.

20 parts of the compound thus obtained whose cation is identical with that of rhodamine 6G (C.I. 45,160) is dissolved at 90° to 95°C in a solution of 15 parts of a urea-formaldehyde condensation product and 65 parts of diethylene glycol to form a red ball point pen ink. This ink has good writing qualities and very good storage stability.

EXAMPLE 10

8 parts of the compound obtained according to Example 9 is dissolved in a solution of 36 parts of a phthalic acid hexanetriol ester and 54 parts of dipropylene glycol. A glycol printing ink which keeps well, which is practically non-corrosive and which gives prints which are fast to water is obtained.

A flexographic printing ink which keeps very well is similarly obtained from 5 parts of rhodamine 6G ethyl ester phosphate and 25 parts of shellac by dissolving them in 90 parts of commercial ethanol and 10 parts of ethylene glycol monoethyl ether at room temperature. The water fastness of prints prepared therewith is better than when commercial rhodamine 6G ethyl ester chloride (C.I. 45,160) is used for its production.

Similar results are achieved by using the following dyes: rhodamine 6G methyl ester phosphate, rhodamine 6G borate and rhodamine 6B methyl ester borate.

EXAMPLE 11

After the dye solution of rhodamine 6G methyl ester sulfate obtained according to Example 9 has been clarified by filtration at 65° to 70°C, 5.2 parts of sodium bicarbonate is added to it with good stirring. The dye is precipitated as the bicarbonate salt. It is filtered off, washed and dried at 70°C. 11.5 parts of rhodamine 6G methyl ester bicarbonate is obtained.

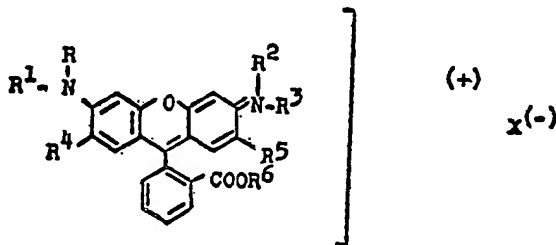
| Analysis: | C% | H% | O% | N% | CO ₂ % |
|---|------|-----|------|-----|-------------------|
| | 66.7 | 6.5 | 21.8 | 5.2 | 8.3 |
| | 66.1 | 6.6 | 22.0 | 5.3 | 7.9 |
| Calculated as C ₂₈ H ₃₀ N ₂ O ₆ | 68.6 | 6.1 | 19.6 | 5.7 | 9.0 |

10 parts of the dye thus obtained is dissolved while heating at 80° to 90°C in a mixture of 50 parts of diethylene glycol monobutyl ether, 18 parts of oleic acid, 15 parts of mineral oil and 17 parts of a colophony resin. This glycol printing ink containing mineral oil is distinguished by only a slight tendency to corrode and good storage stability and results in prints having good water fastness.

The corresponding rhodamine 6G ethyl ester bicarbonate is also a valuable compound within the scope of the present invention.

WHAT WE CLAIM IS:—

1. A rhodamine dye which is sparingly soluble or insoluble in water and has the general formula:—



in which

R denotes a hydrogen atom, methyl group or ethyl group;

R¹ denotes a hydrogen atom, methyl group or ethyl group;

R^2 denotes a hydrogen atom, methyl group or ethyl group;

R^2 denotes a hydrogen atom, methyl group or ethyl group;

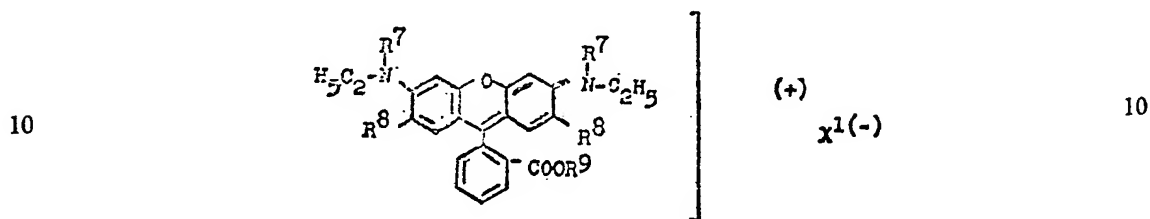
R^1 denotes a hydrogen atom or methyl group;

R^3 denotes a hydrogen atom or methyl group;

5 R^4 denotes a hydrogen atom, methyl group or ethyl group; and

$X^{(-)}$ denotes the anion of a sulfuric acid monoester or of an aliphatic sulfonic acid or a benzene sulfonate, toluene sulfonate, xylene sulfonate, $\text{NO}_3^{(-)}$, $\text{H}_2\text{BO}_3^{(-)}$, $\text{HCO}_3^{(-)}$, $\text{H}_2\text{PO}_4^{(-)}$, $\text{HCrO}_4^{(-)}$ or $\text{HCr}_2\text{O}_7^{(-)}$ anion.

2. A rhodamine dye having the general formula: —



in which R^9 denotes a hydrogen atom, methyl or ethyl group;

R^7 denotes a hydrogen atom or ethyl group;

R^8 denotes a hydrogen atom or a methyl group; and

$X^{(-)}$ denotes one of the anions: $\text{NO}_3^{(-)}$, $\text{HCO}_3^{(-)}$, $\text{H}_2\text{OBO}_3^{(-)}$, and $\text{H}_2\text{PO}_4^{(-)}$.

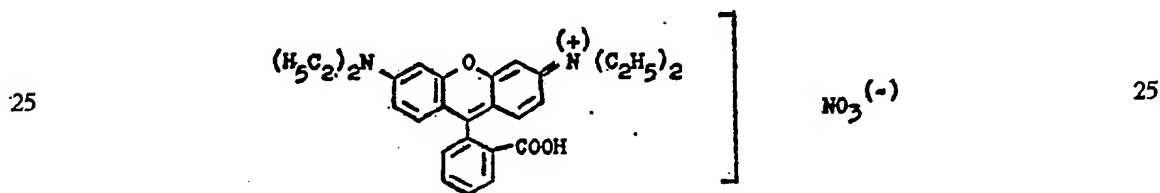
15 3. A rhodamine dye having the general formula depicted in claim 1 in which R^1 to R^6 inclusive have the meanings specified in claim 1 and $X^{(-)}$ denotes one of the anions: $\text{CH}_3\text{OSO}_3^{(-)}$, $\text{C}_6\text{H}_5\text{SO}_3^{(-)}$, $\text{CH}_3\text{CH}_2\text{OSO}_3^{(-)}$ and $\text{CH}_3\text{C}_6\text{H}_4\text{SO}_3^{(-)}$.

4. A rhodamine dye as claimed in claim 1 in which not more than one of R^2 , R^3 and R^5 and not more than one of R , R^1 and R^4 denote hydrogen.

20 5. A rhodamine dye as claimed in claim 1 in which R^2 and R^3 each denote a methyl group or an ethyl group.

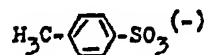
6. A rhodamine dye as claimed in claim 1 in which R^1 and R^5 each denote a methyl group.

7. The dye having the formula: —



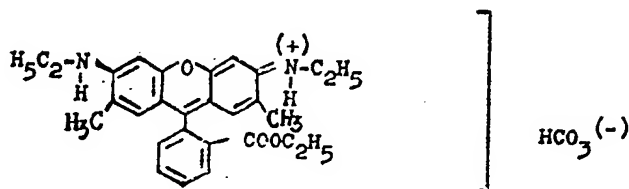
8. The dye having the cation according to the formula in claim 7 and having $\text{H}_2\text{BO}_3^{(-)}$ as the anion.

9. The dye having the cation according to the formula in claim 7 and having



30 as the anion.

10. The dye having the formula: —



11. The dye having the cation according to the formula in claim 10 and having $C_2H_5OSO_3^{(-)}$ as the anion.
12. The dye having the cation according to the formula in claim 10 and having $CH_3OSO_3^{(-)}$ as the anion.
- 5 13. A dye claimed in claim 1 and as specified in any of the foregoing Examples. 5
14. A process for the production of a dye claimed in any of claims 1 to 13 wherein a rhodamine dye chloride or sulfate is reacted with an alkali metal salt of an anion $X^{(-)}$ which has one of the meanings specified in claim 1.
- 10 15. A process as claimed in claim 14 carried out substantially as described in any of the foregoing Examples. 10
16. Dyes when obtained by a process claimed in claim 14 or 15.
17. A process for the production of a printing ink, stamping ink, marking ink, ball point pen ink or transparent surface coating in which a compound as claimed in any of claims 1 to 13 or 16 is employed as a dye.
- 15 18. A product of a process claimed in claim 17. 15

J. Y. & G. W. JOHNSON,
Furnival House,
14—18, High Holborn,
London, W.C.1.
Chartered Patent Agents,
Agents for the Applicants.

Printed for Her Majesty's Stationery Office, by the Courier Press, Leamington Spa. 1971.
Published by The Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from
which copies may be obtained.

THIS PAGE BLANK (USPTO)